



## Surface Tension of Binary Liquid Mixtures at 298.15, 303.15 and 313.15 K

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### Abstract

Densities and surface tensions were measured for the binary liquid mixtures formed by benzonitrile, and benzyl alcohol with benzene at 298.15, 303.15 and 313.15 K and atmospheric pressure over the whole concentration range. Prigogine-Flory-Patterson model (PFP), Ramaswamy and Anbananthan (RS), model derived by Glinski, Sanchez equation, Goldsack relation and Eberhart models were utilized to predict the associational behavior of weakly interacting liquids. The measured properties were fitted to Redlich-Kister polynomial relation to estimate the binary coefficients and standard errors. Furthermore, McAllister multi body interaction model was also used to correlate the binary properties. These non-associated and associated models were compared and tested for different systems showing that the associated processes yield fair agreement between theory and experiment as compared to non-associated processes.

**Keywords:** Surface Tension, Binary Prigogine-Flory-Patterson, McAllister, Sanchez, Eberhart

### Introduction

Prediction of surface tension is of outstanding importance in many scientific and technological areas such as liquid-liquid extraction, gas absorption, distillation, condensation, environmental sciences, material sciences, process simulation, molecular dynamics etc and play a significant role in several industries such as paints, detergents, agrochemicals and petroleum. As a fundamental parameter, surface tension is the single most accessible experimental parameter that describes the thermodynamic state and contains at least implicit information on the internal structure of a liquid interface. Apart from this theoretical interest, a detailed understanding of the behavior of a vapor-liquid interface, such as enrichment of one component in a liquid surface is important for modeling a distillation process.

Surface tensions have been measured for a long time and collections of experimental data for pure, binary and multi component liquid mixtures<sup>1-4</sup>. A critical review reveals that systematic theoretical and experimental investigations of vapor-liquid interfaces for the prediction of associational behavior are rare, especially in a wide temperature and concentration range. High quality of experimental data of surface tensions forms the basis for a successful modeling and for theoretical calculations of surface properties<sup>5-6</sup>.

In continuation of our work, we present the experimental data on density and surface tension of binary liquid mixtures formed by benzonitrile and benzyl alcohol with benzene at 298.15, 303.15 and 313.15 K and atmospheric pressure over

the whole concentration range. These data were analyzed in terms of Ramaswamy and Anbananthan (RS) model model derived by Glinski, Prigogine-Flory-Patterson (PFP) model, Sanchez model, Goldsack model and Eberhart Model<sup>7-14</sup>. First two models, RS and model devised by Glinski (associated) are based on the association constant as an adjustable parameters where as PFP and others (non-associated) are based the additivity of liquids. For that purposes, we selected the liquids containing poor interacting properties. From these results, deviations in surface tension,  $\Delta\sigma$  were calculated and fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and the standard errors<sup>13</sup>. An attempt has also been made to correlate the experimental data with the McAllister multi body interaction model. This is our first attempt to correlate all the models (associated and non-associated) simultaneously in predicting the associational behavior of binary liquid mixtures from surface tension data.

### Material and Methods

High purity and AR grade samples of benzonitrile, and benzyl alcohol with benzene at 298.15, 303.15 and 313.15 K used in this experiment were obtained from Merck Co. Inc., Germany and purified by distillation in which the middle fraction was collected. The liquids were stored in dark bottles over 0.4nm molecular sieves to reduce water content and were partially degassed with a vacuum pump. The purity of each compound was checked by gas chromatography and the results indicated that the mole fraction purity was higher than 0.99. The purity of chemicals used was confirmed by comparing the densities

and viscosities with those reported in the literature as shown in table 1.

**Apparatus and Procedure:** Before each series of experiments, we calibrated the instrument at atmospheric pressure with doubly distilled water. The uncertainty in the density measurement was within  $\pm 0.5 \text{ kg.m}^{-3}$ . The densities of the pure components and their mixtures were measured with the bi-capillary pycnometer. The average uncertainty in the composition of the mixtures was estimated to be less than  $\pm 0.0001$ .

Surface tension was measured by the differential capillary rise method. A well stirred water bath (Raga Industries) was used with temperature control to  $\pm 0.01 \text{ K}$ . The diameters of the precision bore capillaries were confirmed at several points along the length of each capillary by mercury weighing. The diameter of the capillaries were found to be 0.01 and 0.02 cm. At equilibrium, the difference in the level of menisci in both the capillaries,  $h$ , was constant within the precision of the cathetometer,  $\pm 0.001 \text{ cm}$ . Each experiment was repeated three times at each temperature for all compositions and results were averaged. The estimated uncertainty in surface tension measurements was within  $\pm 1.9 \times 10^{-4} \text{ Nm}^{-1}$ . The surface tension of the mixture,  $\sigma$ , was calculated using the relation;

$$\sigma = \frac{r_1 r_2 \rho g [3\Delta h - (r_2 - r_1)]}{6(r_2 - r_1)} \quad (1)$$

where  $r_1$  and  $r_2$  are the radii  $i$  of the capillaries,  $g$  is the gravitational acceleration and  $\rho$ , the density of the mixture. The angle of contact was assumed to be zero, which was supported by visual observations. The results are listed in table 1 together with literature values for comparison<sup>15</sup>.

**Modeling:** Ramswamy and Anbananthan proposed the model based on the assumption of linearity of acoustic impedance with the mole fraction of components<sup>7</sup>. Further it is assumed, that an equilibrium physical property such as viscosity, refractive index, surface tension etc which are based on linearity can be predicted<sup>11-14</sup>. Further Glinski assumed that when solute is added to solvent the molecules interact according to the equilibrium as:



By applying the condition of linearity with composition

$$\sigma_{\text{obs}} = x_A \sigma_A + x_{AB} \sigma_{AB} \quad (3)$$

Where  $x_A$ ,  $x_{AB}$ ,  $\sigma_A$  and  $\sigma_{AB}$  and  $\sigma_{\text{obs}}$  are the mole fraction of A, mole fraction of associate AB, surface tension of A, surface tension of associate AB and observed surface tension respectively. The component AB can not be obtained in its pure form. Following simplifications have been made, firstly, concentration term should be replaced by activities for concentrated solution and second, there are also molecules of non associated components in the liquid mixture. The eq (3) takes the form,

$$\sigma_{\text{obs}} = [x_A \sigma_A + x_B \sigma_B + x_{AB} \sigma_{AB}] \theta \quad (4)$$

where  $\theta$  is a temperature dependent adjustable parameter which changes with the changing temperature conditions. The general idea of this model can be, however, exploited as;

$$K_{as} = \frac{[AB]}{(C_A - [AB])(C_B - [AB])} \quad (5)$$

where  $C_A$  and  $C_B$  are initial molar concentrations of the components. One can take any value of  $K_{as}$  and calculate the equilibrium value of  $[AB]$  for every composition of the mixture as well as  $[A] = C_A - [AB]$  and  $[B] = C_B - [AB]$ . Replacing molar concentration by activities for concentrated solution, eq (5) becomes,

$$K_{as} = \frac{a_{AB}}{(a_A - a_{AB})(a_B - a_{AB})} \quad (6)$$

where  $a_A$ ,  $a_B$  and  $a_{AB}$  are the activity of component A, Component B and associate, AB respectively. Taking equimolar activities which are equal to;

$$a'_A = a_A - a_{AB} \text{ and } a'_B = a_B - a_{AB} \quad (7)$$

where  $a'_A$  and  $a'_B$  are the activities of [A] and [B] in equimolar quantities respectively.

From eq (7) one can obtain the value of  $K_{as}$  as;

$$K_{as} = \frac{a_{AB}}{a_A a_B - a_A a_{AB} - a_B a_{AB} + a_{AB}^2} = \frac{a_{AB}}{a'_A \cdot a'_B} \quad (8)$$

Now, assuming any value of surface tension in the pure component AB,  $\sigma_{AB}$ , it is possible to compare the surface tension calculated using eq (4) with the experimental values. On changing both the adjustable parameters  $K_{as}$  and  $\sigma_{AB}$  gradually, one can get different values of the sum of squares of deviations,

$$S = \sum (\sigma_{\text{obs}} - \sigma_{\text{cal}})^2 \quad (9)$$

On inspecting the results obtained from Ramaswamy and Anbananthan model, Glinski suggested the equation assuming additivity with the volume fraction,  $\phi$  as;

$$\sigma_{\text{cal}} = \frac{\sigma_1 \sigma_2}{\phi_1 \sigma_2 + \phi_2 \sigma_1} \quad (10)$$

Where  $\sigma_{\text{cal}}$  is the theoretical surface tension of binary liquid mixture,  $\phi_1$ ,  $\phi_2$  are the volume fractions of component 1 and 2 and  $\sigma_1$  and  $\sigma_2$  are the surface tensions of pure component liquids. The numerical procedure and determination of association constant,  $K_{as}$ , were similar to that described before. Flory and collaborators used the cell partition function of Hirschfelder and Eyring and a simple Van der Waals energy- volume relation, by putting  $m=3$ ,  $n \rightarrow \infty$  so that the Flory equations for the mixing functions and partial molar quantities may be obtained from the general corresponding states equations given by making this particular choice of (m,n). Patterson et al have drawn attention to the close connection between the Flory theory and corresponding state theory of Prigogine employing a

simple cell model of the liquid state<sup>11</sup>. The equation of state for the materials conforming to the principle of corresponding states can be expressed in a universal form through the use of suitable characteristic values i.e. (reduction parameters) P,V,T for the pressure, volume and temperature respectively.

In order to extend corresponding state theory to deal with the surface tension, Patterson and Rastogi<sup>11</sup> used the reduction parameters as,

$$\sigma^* = k^{1/3} P^{2/3} T^{1/3} \quad (11)$$

called the characteristic surface tension of the liquid. Here k is the boltzmann constant. Paterson and Rastogi extended the simple cell model theory of the surface tension of spherical molecules by Prigogine and Saraga to the case of chain molecules<sup>16</sup>. A segment experiences an increase in the configurational energy due to the loss of a fraction, M, of its nearest neighbors at the surface while moving from the bulk phase to the surface phase. It's most suitable value ranges from 0.25 to 0.29. In the present case the value of M is taken as 0.29 throughout the calculation. The cell partition function of a segment at the surface is increased due to the loss of constraining nearest neighbors in one direction. With the particular (3,∞) choice of m,n potential, the Flory model takes the form as;

$$\sigma(\bar{V}) = [M \bar{V}^{-5/3} - (\frac{\bar{V}^{1/3} - 1.0}{\bar{V}^2}) \ln(\frac{\bar{V}^{1/3} - 0.5}{\bar{V}^{1/3} - 1.0})]$$

Thus on the basis of flory theory, surface tension of liquid mixture is given by the expression,

$$\sigma = \sigma^* \bar{\sigma}(\bar{V}) \quad (13)$$

All the notations used in the above equations have their usual significance as detailed out by Flory. The relationship between surface tensionσ, isothermal compressibility, β<sub>T</sub>, and density, ρ of a liquid was obtained by Sanchez and applied successfully to binary liquids<sup>12</sup>.

$$\sigma(\beta_T / \rho)^{1/2} = A_0^{1/2} \quad (14)$$

Goldsack and Sarvas used the mole fraction and volume fraction statistics to obtain the expression surface tension and applied to various systems as;

$$x_i, S = x_{i,B} [(\sigma - \sigma_i) \frac{A_i}{R_T}] = 1 \quad (15)$$

where x<sub>i</sub>, S and x<sub>i</sub>, B are the mole fraction of the component in surface and bulk phase respectively and A<sub>i</sub> is the molar surface area of the component for binary liquids.

Eberhart assumed that the surface tension of binary liquids is a linear function of surface layer mole fractions as;

$$\sigma = y_1 \sigma_1 + y_2 \sigma_2 \quad (16)$$

Using a semi-empirical constant, S, which is defined as the surface enrichment factor for the component having the lower surface tension,

$$S = (y_2 / y_1) / (x_2 / x_1) \quad (17)$$

where y<sub>1</sub> and y<sub>2</sub> are surface mole fractions and x<sub>1</sub> and x<sub>2</sub> are bulk mole fractions and where y<sub>1</sub>+y<sub>2</sub>=1 and x<sub>1</sub>+x<sub>2</sub>=1, σ can be expressed in terms of bulk liquid composition of the mixture.

$$\sigma = (x_1 \sigma_1 + x_2 S \sigma_2) / (x_1 + S x_2) \quad (18)$$

## Results and Discussion

Relations between associations phenomenon in liquids were analyzed earlier by considering van der Waals equation of state which was based only on simple averaged geometrical deviations without analyzing the system in terms of equilibrium<sup>17</sup>. The association phenomenon has been related usually the deviation of different quantities from additivity. Ramaswamy and Anbananthan derived the model based on the assumption of linearity of acoustic impedance with the mole fraction of components which was corrected and tested to predict the associational behavior<sup>8,18</sup>. The quantities analyzed were refractive index, molar volume, viscosity, intermolecular free length and many others<sup>19-22</sup>. Prediction of surface tension from this approach is our first attempt. The results of fittings obtained from the model were utilized properly. The calculations were performed using a computer program which allows fittings easily both the adjustable parameters simultaneously or the parameters were changed manually.

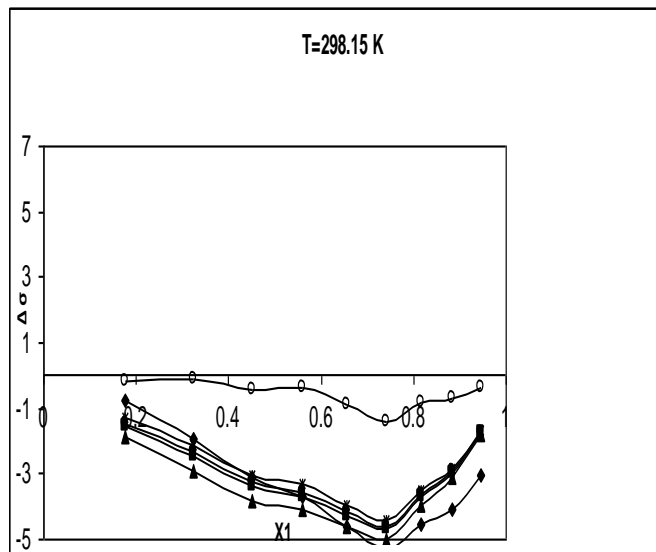
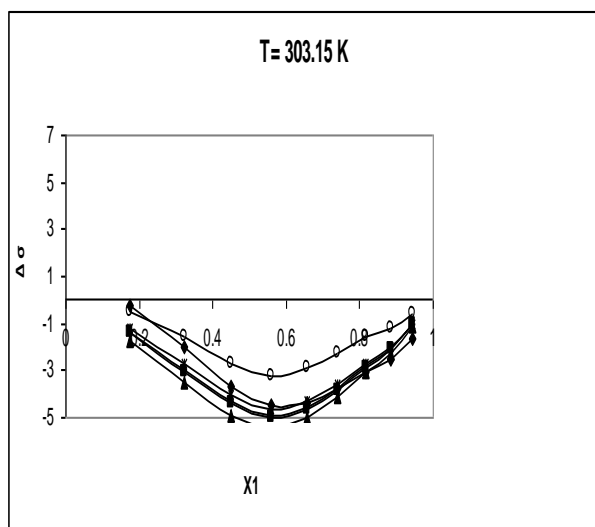
Values of thermal expansion coefficient (α) and isothermal compressibility needed in the PFP model were obtained from the equation which have already been tested in many cases by us<sup>18</sup>. The mixing function Δσ can be represented mathematically by Redlich-Kister polynomial equation for correlating the experimental data as<sup>18</sup>;

$$y = x_i (1 - x_i) \sum_{i=0}^p A_i (2x_i - 1)^i \quad (19)$$

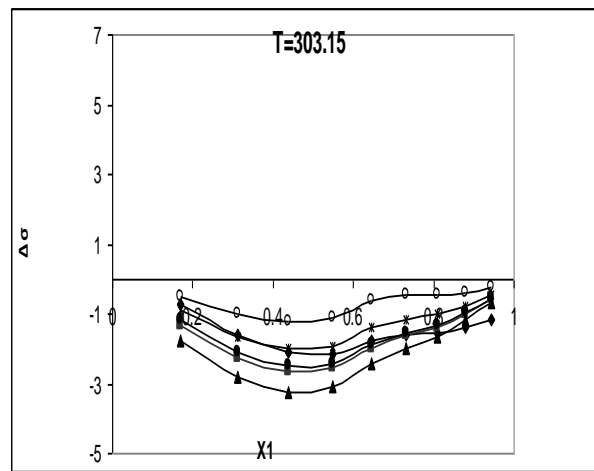
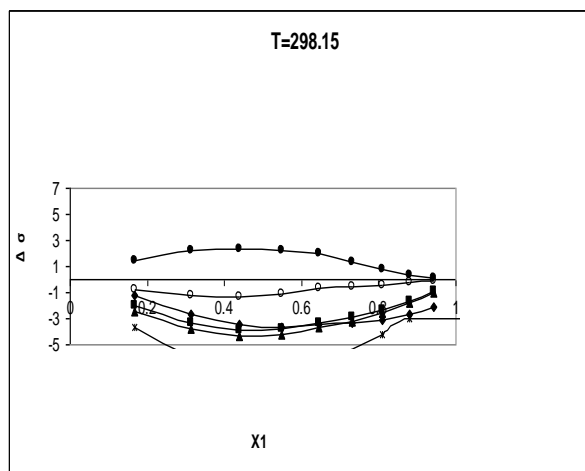
where y refers to deviation in surface tension (Δσ), x<sub>1</sub> is the mole fraction and A<sub>i</sub> is the coefficient. The values of coefficients were determined by a multiple regression analysis based on the least square method and are summarized along with the standard deviations between the experimental and fitted values of the respective function in Table 2. The standard deviation is defined by,

$$\delta = \left[ \sum_{i=1}^m (y_{\text{exp}} - y_{\text{cal}})^2 / (m - p) \right]^{1/2} \quad (20)$$

where m is the number of experimental points and p is the number of adjustable parameters. The values of standard deviation lie 0.0551 to 0.4217. Multibody interaction model of McAllister is widely used for correlating the viscosity of liquid mixtures with mole fraction which is based on the assumption of additivity<sup>19</sup>.



**Bez+Benzonitrile**



**Figure-2**

Plot of surface tension deviations,  $\Delta\sigma$  with mole fraction  $x$ , for benzene + (1-x) benzyl alcohol at 298.15 and 303.15 K and benzene + (1-x) benzonitrile at 298.15 and 303.15 K:  $\blacklozenge$ , PFP(eq.19),  $\blacksquare$ , Sanchez (22),  $\blacktriangle$ , Goldsack and sarvas(eq.25), Eberhart (eq.29),  $*$ , RS(eq.5),  $\bullet$ , model devised by Glinski(eq.10)

**Table-1**

Comparison of density ( $\rho$ ) and Surface tension ( $\sigma$ ) with literature data for pure components at 298.15, 303.15, and 313.15 K

Components	T/K	$\alpha \times 10^{-3}$ K	$\beta \times 10^{12}$ Pa	V/ $\text{cm}^3$ $\text{mole}^{-1}$	$\rho_{\text{exp}} /$ $\text{g.cm}^{-3}$	$\rho_{\text{lit}} /$ $\text{g.cm}^{-3}$	$\sigma_{\text{exp}} /$ $\text{mN.m}^{-1}$	$\sigma$ $/\text{mN.m}^{-1}$ lit
Benzene	298.15	1.218023	94.60978	89.32	0.8732	0.8736 <sup>b</sup>	28.02	28.20 <sup>b</sup>
	303.15	1.21875	94.77915	89.94	0.8680	0.8683 <sup>b</sup>	27.38	27.56 <sup>b</sup>
	313.15	1.24239	100.4023	91.13	0.8575	0.8576 <sup>b</sup>	26.79	-
Benzonitrile	298.15	0.997994	52.04158	103.08	1.0003	1.0006 <sup>b</sup>	38.33	-
	303.15	1.008302	53.67095	103.56	0.9976	0.9978 <sup>b</sup>	38.19	38.38 <sup>b</sup>
	313.15	1.016819	55.04248	105.24	0.9919	-	38.03	-
Benzyl alcohol	298.15	1.015504	54.82925	103.82	1.0412	1.0413 <sup>b</sup>	39.03	-
	303.15	1.021907	55.87294	104.24	1.0376	1.0376 <sup>b</sup>	38.81	38.94 <sup>b</sup>
	313.15	1.063372	62.95392	107.98	1.0366	-	38.31	-

a Ref 23 b Ref 15

**Table-2**  
**Coefficients of the Redlich-Kister equation and standard deviations ( $\sigma$ ) for surface tension of binary liquid mixtures at various temperatures**

**Benzene+Benzonitrile**

	T	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	Std dev( $\delta$ )
$\Delta\sigma/\text{mN.m}^{-1}$	298.15	12.6428	-1.2057	-1.2846	4.9859	0.0551
	303.15	7.5091	-3.5624	-2.5595	8.6404	0.0832
	313.15	4.3350	-0.5640	-4.3693	2.0337	0.1343

**Benzene+Benzylalcohol**

$\Delta\sigma/\text{mN.m}^{-1}$	T	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	Std dev( $\delta$ )
	298.15	12.7894	10.0663	10.0663	0.3097	0.1998
	303.15	17.1911	7.0611	-8.9754	3.8436	0.1620
	313.15	7.5755	4.4203	-2.5178	-1.4961	0.1122

**Table-3**  
**Parameters of McAllister Three body and Four body Interaction Models and Standard Deviations ( $\sigma$ ) for Surface Tension of Binary Liquid Mixtures at Various Temperatures**

Component	Temp	McAllister Three Body ( $\sigma/\text{m N.m}^{-1}$ )			McAllister Four Body ( $\sigma/\text{m N.m}^{-1}$ )			
		a	b	( $\sigma$ )	a	b	c	( $\sigma$ )
Benzene+Benzonitrile	298.15	36.7411	38.7966	0.0873	34.4134	37.4648	38.8202	0.0876
	303.15	33.7796	37.3544	0.1391	31.8587	35.8572	37.2830	0.1325
	313.15	32.2240	35.8585	0.1837	29.8686	36.0244	34.9991	0.1010
Benzene+Benzylalcohol	298.15	42.1778	33.6207	0.4234	29.1982	33.4461	33.0062	0.1825
	303.15	39.5465	35.7636	0.2514	28.3772	33.1275	32.9763	0.1046
	313.15	34.0128	33.7965	0.1125	27.7798	32.6639	31.2272	0.1597

**Table-4**  
**Comparison of absolute average deviation values obtained from various liquid state models**

Component Liquids	Temp (K)	Kas	$\sigma_{\text{ab(RS)}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.4}}/\text{mN.m}^{-1}$	$\sigma_{\text{ab(Glin)}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.10}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.13}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.14}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.15}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.16}}/\text{mN.m}^{-1}$
Benzene+Benzonitrile	298.15	0.9990	37.80	4.87	25.00	1.43	2.86	2.66	2.99	0.72
	303.15	0.0010	37.00	1.25	37.00	1.60	1.57	1.70	2.09	0.66
	313.15	0.0050	36.50	0.64	36.50	0.99	0.94	1.14	1.50	0.38
Benzene+Benzylalcohol	298.15	0.0014	35.00	2.91	35.00	3.08	3.46	3.15	3.47	0.59
	303.15	0.0015	35.10	2.91	35.10	3.09	2.86	3.15	3.46	1.84
	313.15	0.0002	35.30	1.33	35.30	3.37	1.85	1.94	1.86	1.00

**Table -5**  
**Experimental densities ( $\rho$ ), experimental surface tensions ( $\sigma_{exp}$ ), theoretical surface tension from PFP model ( $\sigma_{Eq.19}$ ), Sanchez method, ( $\sigma_{Eq.22}$ ), Goldsack model, ( $\sigma_{Eq.25}$ ), Eberhart model, ( $\sigma_{Eq.29}$ ), RS model ( $\sigma_{Eq.5}$ ), Glinski model ( $\sigma_{Eq.10}$ ) of binary liquid mixtures and their percent deviations ( $\% \Delta \sigma$ ) at various temperatures.**

**Benzene+Benzonitrile**

X1	$\rho/gm.cm^{-3}$	$\sigma_{exp}/mN.m^{-1}$	$\sigma_{Eq.13}/mN.m^{-1}$	$\sigma_{Eq.14}/mN.m^{-1}$	$\sigma_{Eq.15}/mN.m^{-1}$	$\sigma_{Eq.16}/mN.m^{-1}$	$\sigma_{Eq.4}/mN.m^{-1}$	$\sigma_{Eq.10}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.13}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.14}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.15}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.16}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.5}/mN.m^{-1}$	$\% \Delta \sigma_{Eq.10}/mN.m^{-1}$
<b>298.15</b>														
0.1681	0.9987	38.20	36.95	36.17	35.81	37.47	34.53	38.32	3.26	5.31	6.26	1.91	9.62	-0.33
0.3126	0.9875	37.78	35.14	34.50	34.02	36.58	31.86	37.78	6.98	8.68	9.96	3.18	15.68	0.01
0.4381	0.9765	37.01	33.56	33.15	32.66	35.65	30.05	36.82	9.33	10.43	11.76	3.67	18.80	0.52
0.5481	0.9645	35.83	32.17	32.05	31.59	34.69	28.89	35.59	10.21	10.56	11.83	3.18	19.36	0.66
0.6453	0.9568	34.40	30.94	31.11	30.72	33.69	28.20	34.24	10.05	9.55	10.69	2.06	18.02	0.46
0.7318	0.9423	33.20	29.85	30.32	30.00	32.65	27.83	32.86	10.09	8.67	9.63	1.66	16.17	1.01
0.8093	0.9356	31.96	28.87	29.63	29.39	31.56	27.69	31.52	9.67	7.30	8.04	1.25	13.35	1.37
0.8792	0.9156	30.66	27.99	29.03	28.87	30.43	27.71	30.26	8.71	5.33	5.84	0.75	9.63	1.31
0.9423	0.8876	29.37	27.23	28.50	28.42	29.25	27.83	29.09	7.32	2.99	3.26	0.41	5.25	0.95
<b>303.15</b>														
0.1681	0.9825	37.26	36.54	35.95	35.51	36.78	36.37	36.07	1.94	3.51	4.68	1.28	2.39	3.19
0.3126	0.9758	36.45	34.82	34.20	33.63	35.47	34.80	34.36	4.46	6.17	7.75	2.69	4.51	5.74
0.4381	0.9678	35.43	33.33	32.79	32.20	34.23	33.45	32.95	5.95	7.46	9.12	3.39	5.60	7.00
0.5481	0.9587	34.18	32.01	31.63	31.09	33.08	32.26	31.77	6.34	7.47	9.04	3.22	5.62	7.06
0.6453	0.9564	32.61	30.85	30.64	30.18	31.99	31.21	30.76	5.40	6.02	7.43	1.90	4.30	5.67
0.7318	0.9356	31.43	29.81	29.81	29.43	30.96	30.27	29.90	5.15	5.17	6.35	1.50	3.68	4.88
0.8093	0.9152	30.46	28.89	29.08	28.80	29.99	29.44	29.15	5.17	4.54	5.45	1.54	3.36	4.32
0.8792	0.9056	29.44	28.05	28.44	28.26	29.07	28.68	28.48	4.72	3.40	4.02	1.26	2.57	3.24
0.9423	0.8768	28.46	27.30	27.88	27.79	28.21	28.00	27.90	4.06	2.02	2.33	0.88	1.61	1.96
<b>313.15</b>														
0.1681	0.9642	36.49	36.31	35.66	35.25	36.32	36.12	35.82	0.48	2.27	3.39	0.47	1.01	1.83
0.3126	0.9523	35.19	34.53	33.82	33.28	34.79	34.49	34.04	1.87	3.89	5.42	1.14	2.00	3.26
0.4381	0.9487	34.13	32.98	32.35	31.81	33.43	33.07	32.58	3.35	5.20	6.80	2.05	3.10	4.55
0.5481	0.9356	33.20	31.62	31.14	30.64	32.20	31.83	31.35	4.75	6.19	7.68	3.01	4.11	5.58
0.6453	0.9365	31.62	30.41	30.13	29.70	31.08	30.74	30.30	3.82	4.72	6.06	1.71	2.77	4.17
0.7318	0.9136	30.45	29.34	29.27	28.93	30.07	29.78	29.40	3.64	3.88	5.00	1.25	2.21	3.43
0.8093	0.9	29.31	28.38	28.52	28.27	29.14	28.91	28.62	3.17	2.70	3.56	0.58	1.36	2.34
0.8792	0.8865	28.34	27.52	27.87	27.71	28.29	28.13	27.94	2.90	1.66	2.25	0.18	0.73	1.42
0.9423	0.8658	27.56	26.75	27.30	27.22	27.51	27.43	27.33	2.97	0.95	1.25	0.18	0.47	0.83

### Benzene+Benzylalcohol

X1	$\rho/\text{gm. cm}^{-3}$	$\sigma_{\text{exp}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.13}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.14}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.15}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.16}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.4}}/\text{mN.m}^{-1}$	$\sigma_{\text{Eq.10}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.13}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.14}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.15}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.16}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.5}}/\text{mN.m}^{-1}$	$\% \Delta \sigma_{\text{Eq.10}}/\text{mN.m}^{-1}$
<b>298.15</b>														
0.1749	1.0008	36.54	35.75	34.99	34.67	36.36	35.23	35.09	2.16	4.23	5.12	0.48	3.58	3.97
0.3229	0.9935	36.04	34.11	33.60	33.15	35.91	33.94	33.72	5.35	6.78	8.01	0.37	5.84	6.44
0.4498	0.9825	35.84	32.70	32.46	32.00	35.39	32.82	32.58	8.77	9.42	10.72	1.27	8.42	9.09
0.5598	0.9601	35.19	31.47	31.52	31.08	34.79	31.86	31.62	10.58	10.42	11.67	1.14	9.46	10.13
0.6561	0.9445	34.98	30.38	30.72	30.34	34.10	31.02	30.81	13.14	12.17	13.27	2.51	11.32	11.94
0.741	0.9236	34.70	29.43	30.04	29.72	33.30	30.28	30.10	15.20	13.44	14.34	4.03	12.74	13.26
0.8166	0.9001	33.14	28.57	29.44	29.20	32.34	29.62	29.48	13.79	11.19	11.90	2.41	10.63	11.05
0.8841	0.8935	31.87	27.81	28.91	28.75	31.20	29.03	28.93	12.73	9.28	9.78	2.10	8.91	9.21
0.945	0.8801	30.19	27.12	28.44	28.36	29.79	28.50	28.45	10.15	5.79	6.05	1.33	5.60	5.76
<b>303.15</b>														
0.1749	0.9998	35.75	35.53	34.34	34.02	35.25	34.57	34.41	0.62	3.95	4.84	1.40	3.30	3.74
0.3229	0.9874	35.99	33.95	32.95	32.51	34.39	33.28	33.05	5.68	8.46	9.68	4.45	7.54	8.18
0.4498	0.9754	36.23	32.59	31.82	31.36	33.53	32.17	31.91	10.06	12.18	13.46	7.45	11.21	11.92
0.5598	0.9564	35.87	31.40	30.88	30.45	32.67	31.21	30.96	12.46	13.91	15.12	8.92	13.00	13.70
0.6561	0.9354	34.70	30.36	30.08	29.70	31.80	30.37	30.14	12.52	13.31	14.40	8.36	12.48	13.14
0.741	0.9002	33.23	29.43	29.39	29.08	30.93	29.63	29.44	11.42	11.53	12.47	6.92	10.83	11.41
0.8166	0.8897	31.65	28.61	28.79	28.56	30.05	28.97	28.83	9.59	9.01	9.75	5.06	8.46	8.93
0.8841	0.8845	30.36	27.88	28.27	28.11	29.16	28.39	28.29	8.19	6.90	7.42	3.95	6.50	6.83
0.945	0.8789	28.87	27.21	27.80	27.72	28.27	27.86	27.81	5.75	3.72	3.99	2.08	3.51	3.68
<b>313.15</b>														
0.1749	0.9745	34.54	33.62	29.91	33.41	34.19	33.94	16.94	2.67	13.39	3.26	1.01	1.73	50.96
0.3229	0.9683	33.84	32.29	32.41	31.92	33.04	32.66	32.45	4.59	4.23	5.68	2.36	3.49	4.11
0.4498	0.9512	33.38	31.14	31.29	30.78	32.01	31.56	31.32	6.70	6.24	7.79	4.10	5.46	6.16
0.5598	0.9354	32.73	30.13	30.35	29.86	31.06	30.61	30.37	7.93	7.27	8.76	5.10	6.49	7.20
0.6561	0.9102	31.67	29.25	29.54	29.12	30.20	29.77	29.56	7.64	6.70	8.04	4.64	6.00	6.66
0.741	0.8754	30.60	28.46	28.85	28.50	29.40	29.03	28.86	7.01	5.74	6.87	3.92	5.12	5.70
0.8166	0.8563	29.70	27.75	28.24	27.98	28.67	28.38	28.24	6.56	4.93	5.81	3.47	4.45	4.91
0.8841	0.8365	28.84	27.12	27.70	27.53	28.00	27.79	27.70	5.94	3.95	4.55	2.91	3.63	3.95
0.945	0.8236	27.67	26.55	27.22	27.13	27.37	27.27	27.22	4.03	1.63	1.94	1.08	1.46	1.63

The coefficients a,b, and c were calculated using the least square procedure and the results of estimated parameters and standard deviation between the calculated and experimental values are presented in table 3. It is observed that four body model is correlated the mixture surface tension to a significantly higher degree of accuracy for all the systems than the three body model. Generally McAllister model is adequate in correlating the systems having small deviations. Mixture data are presented in table 4-5.

With the increase of mole fraction, the values of surface tension obtained from all the models decrease at all temperatures except at few places. The absolute average deviations (AAD) in surface tension obtained from different models are provided in table 4 It is observed that all the equations are equally good and provide fairly good results. Higher deviation values in PFP model (eq 13) can be explained as the model was developed for non-electrolyte  $\gamma$ -meric spherical chain molecules and the system under investigation have interacting and associating properties. Moreover, the expression used for the computation of  $\alpha$  and  $\beta_T$  are also empirical in nature.

### Conclusion

Associated process give more reliable results as compared to non-associated processes and helpful in deducing the internal structure of associates through the fitted values of

surface tension in a hypothetical pure associate and observed dependence of concentration on composition of a mixture.

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